Coagulation of Colloidal Particles in Water by Chitosan

Chihpin Huang* & Yin Chen

Institute of Environmental Engineering, National Chiao Tung University, 75 po-ai st., Hsinchu, Taiwan 30039

Abstract: The feasibility of applying chitosan, as prepared from the crab chitin, was assessed in this study for the coagulation of colloidal particles. A series of batch flocculation tests with chitosan under different conditions was also conducted. The results indicate that chitosan is a potent coagulant for bentonite suspension. The relationship between the optimum chitosan dosage and the turbidity of the bentonite suspension is presented as a linear correlation. The evidence infers that an adequate range of the coagulant dosage is the primary consideration in determining the removal efficiency for the turbidity of the source water. It also indicates that the coagulation behavior for kaolinite by chitosan is different from that of bentonite, i.e., chitosan fails to form a good aggregate with kaolinite. Turbid water containing particles which show behavior similar to kaolinite apparently need to have some bentonite particles added as coagulant aid, thereby improving the aggregation of the colloid particles with chitosan. Moreover, the effect of pH on the coagulation efficiency of chitosan is insignificant. The evidence infers that charge neutralization is not a major mechanism controlling the formation of floc for chitosan coagulation.

Key words: coagulation, flocculation, chitosan, bentonite, kaolinite.

1 INTRODUCTION

Water treatment plants in Taiwan widely use aluminum sulfate or polyaluminum sulfate as a coagulant to remove turbidity from source waters. However, the use of such chemicals decreases the alkalinity of water, has a strong pH-dependence for effective coagulation, causes secondary pollution in the sludge disposal, and has raised public health concerns owing to the amount of aluminum remaining in the treated water.[1–3] To minimize these drawbacks, polymers combined with alum or polymers alone is the latest development in physical–chemical water treatment in USA. The coagulation of negatively charged solids with polymers has already received extensive attention.[4–8] However, it is contended that the residual polyacrylamide in treated water may cause neurological disorders in humans.[9–11] Therefore, biopolymers have the potential of substituting for polyelectrolytes as coagulants in water treatment, however the feasibility of using biopolymers in

coagulation has received scarce limited attention until now.

Parazak *et al.*[12] indicated that the capability of cationic polyelectrolytes to coagulate negatively charged particles was not only produced by bridging or electrostatic patch flocculation, but also that a part of the coagulation energy arose from the hydrophobic interaction of polymer molecules with adjacent particles. This mechanism is referred to as hydrophobic flocculation. Domard *et al.*[13] investigated the adsorption of chitosan on kaolinite. Their investigation has demonstrated that the adsorption behavior of chitosan and kaolinite can be described by the Langmuir equation. Furthermore, more deacetylated or higher molecular weight chitosan would result in a better adsorption capacity of kaolinite. In a similar work, Kawamura[14] suggested that natural products such as chitosan and sodium alginate were potent substitutes for synthetic products.

In this study, the feasibility of using chitosan for coagulation in water treatment was assessed. Two common particles, bentonite and kaolinite, were used as

* To whom correspondence should be addressed.

model particles. A series of tests, including the effect of pH was also conducted. Moreover, an approach to understand the possible mechansims responsible for the coagulation between chitosan and particles was proposed by measuring the zeta-potential on the aggregate. Finally, the relationship between optimal dosages and various turbidities of source water was classified to provide preliminary data for plant operations.

2 MATERIALS AND METHODS

2.1 Synthetic and natural suspension

A given amount of bentonite (Hayashi Co., Japan) or kaolinite (Nakarai Co., Japan) in powder form was added to a solution containing 10^{-2} M $NaClO_4$ electrolyte to prepare a test suspension with the desired turbidity. A raw sample from the Hsinchu water treatment plant in Taiwan was used as a natural suspension to compare its coagulation behavior with synthetic suspensions. Prior to the experiment, strong mixing was carried out for 3 h to homogenize the suspension. The turbidity measurements of the suspension, measured by the standard nephelometry procedure with a turbiditimeter (HACH Ratio, USA), are reported in nephelometric turbidity units (NTU). Two hundred mg of bentonite in 1 dm^3 $NaClO_4$ solution was measured as being 30 NTU and similarly, a 50 mg/dm^{-3} kaolinite suspension was found to be equivalent to 25 NTU.

2.2 Preparation of chitosan solution

Chitin isolated from a crab shell was crushed to a powder form. Chitosan was prepared by deacetylating chitin with NaOH (45%, w/w) at 100°C for 20 min. Thereafter, the product was cleaned several times by deionized water until the pH value of the chitosan suspension reached 7, and was then dried at 80°C for 48 h. The sheet of deacetylated chitin was then crushed to a powdered form and sieved through 50/100 meshes to obtain the powder. Two (dry wt) of chitosan powder was dissolved in 200 cm^3 of acetic acid (1·0%) solution to yield a 1·0% stock solution by agitation at approximately 100 rpm with a magnetic stirrer until the solution was completely dissolved. It was necessary to heat this stock solution to accelerate the dissolution; however, prolonged heating should be avoided. The test reagents were prepared by diluting the stock reagent to a desired concentration just prior to the addition.

2.3 Jar testing

Coagulation–flocculation–sedimentation process piloting usually involves the use of bench-scale test equipment (jar testing) for the studies dealing with unit processes utilized for turbidity (i.e. particulate) removal. A conventional jar test apparatus (Phips and Bird, USA) was used in the experiments. The pH value was adjusted by adding a strong base (0·1 M NaOH) or strong acid (0·1 M $HClO_4$) to the suspension throughout the experiment. The tests were performed by adding the chitosan reagent to the turbid samples, followed by mixing at 100 rpm for 2 min, and thereafter mixing at 30 rpm for 20 min. The aggregates were allowed to settle for 10 min before taking a sample from the top inch of the supernatant for turbidity measurements. Once the sample was taken for turbidity measurement, the jars were stirred gently and coagulated particles in the jar were taken to measure their zeta-potential with a zeter meter (System 3.0, Zeter-Meter Inc., USA). The settling characteristic of the chitosan floc was measured by the settled floc-volume. The height of the floc-volume in the sediment was measured after settling for 30 min in a 1 dm^3 graduated cylinder.

3 RESULTS AND DISCUSSION

3.1 Jar-mixing/settling for bentonite suspensions

In this study, the residual turbidities of supernatants after jar-mixing/settling were conducted at pH 4 with various chitosan dosages for a wide range of initial turbidities (including 30, 90, 150, 400 and 600 NTU). A typical result a 30 NTU bentonite suspension is shown in Fig. 1. An increase in dosage would cause a decrease in the residual turbidity from the initial value of 30 NTU down to a minimum of 0·56 NTU. This occurrence indicates that chitosan is a potent coagulant for bentonite suspension. Once the chitosan dosage exceeds the saturation of polymer bridging, surplus chitosan has a tendency to destroy the polymer bridging between particles, thereby exhibiting an increase in residual turbidity. Results obtained from bentonite suspensions with initial turbidities of 90, 150, 400 and 600 NTU also have a similar trend to the residual turbidities Weber[15] indicated that polymer overdosing produces restabilized particles, since no sites are available for the formation of bridges, resulting in the steric repulsion.

Figure 1 shows the zeta-potential of coagulated particles corresponding to the various dosages of chitosan. As expected, the negative zeta-potential of coagulated particles decreases as the dosage of positively-charged chitosan increases. It indicates that when the chitosan coagulation reaches the optimal state (around a chitosan dosage of 1 mg dm^{-3}), in which the residual turbidity of the supernatant after jar-mixing/settling is the lowest, the surface of bentonite still has a negative charge. Chitosan, like a cationic polymer, can destabilize the colloidal particles through adsorption and interparticle bridging.[15] Therefore, it is unnecessary to
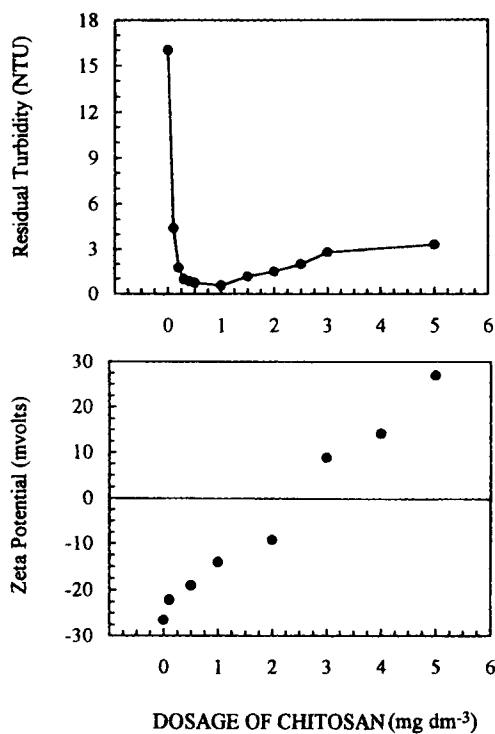
Fig. 1. The residual turbidities of supernatants after jar-mixing/settling and the zeta-potential of coagulated particles with various chitosan dosages for an initial turbidity of 30 NTU at pH 4.

DOSAGE OF CHITOSAN (mg dm⁻³)

Fig. 2. The residual turbidities of supernatants after jar-mixing/settling, showing the zeta-potential of coagulated particles with various chitosan dosages for an initial turbidity of 30 NTU at pH 7. Inset diagram: zeta-potentials of chitosan vs pH.

DOSAGE OF CHITOSAN (mg dm⁻³)

neutralize the surface charge of particles if the aggregation is mostly caused by interparticle bridging. However, the results also indicate that overdosing of chitosan beyond the optimal state (i.e. chitosan dosage of more than 2 mg dm^{-3}) causes the reversal of surface charge as well as the restabilization of coagulated particles. Dosages of chitosan which are sufficiently large to saturate the colloidal surfaces produce restabilized colloids and, under extended agitation, the breaking of polymer–surface bonds and subsequently folding back of extended segments onto the surface of the particles, thereby resulting in the positive zeta-potential of coagulated particles.

Following the same procedure as used at pH 4, the residual turbidities of supernatants after jar-mixing/settling were also investigated at pH 7 with various chitosan dosages and a wide range of initial turbidities. A typical result for 30 NTU is presented in Fig. 2. This figure shows that the trend of residual turbidity at pH 7 is similar to that at pH 4. However, results obtained from zeta-potentials at pH 7 are quite different from those at pH 4. These results indicate that coagulated particles cause negative charges within a wide dosage range from a small quantity to 10 mg dm^{-3}; in addition, the reversal is absent as overdosing of chitosan coagulant occurs. The isoelectric point of chitosan is about 8·7 according to results obtained from plotting zeta-potentials of chitosan vs pH, as shown in the inset of Fig. 2. When pH values shift from 4 to 7, the positive
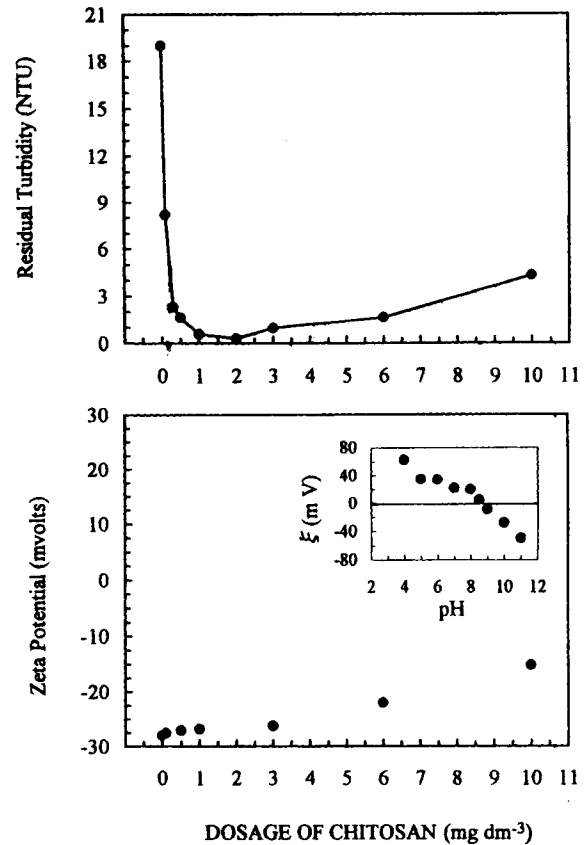
charge on the chitosan surface significantly decreases. From this evidence, we can infer that by introducing chitosan as a coagulant reagent for bentonite suspensions, the contribution of the charge neutralization of chitosan to destabilize clay particles is less significant with an increase in pH value. Therefore, the bridging flocculation is the major mechanism for chitosan to destabilize the colloid particles in the neutral condition (pH $\approx$ 7). Hence, we suggest that chitosan is a potent coagulant for bentonite particles, regardless of the pH value of the solution.

3.2 Optimal dosage of chitosan for bentonite suspensions

We also believe that the lowest turbidity in the supernatant after jar-mixing/settling is the optimal dosage condition. Optimal chitosan dosages with respect to various turbidities of bentonite suspensions in the acidic and neutral pH condition are illustrated in Fig. 3. This figure indicates a linear correlation between optimum chitosan dosages and initial turbidities of bentonite suspensions either at pH 4 or pH 7. As is known, the dosages of common coagulants including aluminum sulfate, ferric chloride, and polyaluminum chloride are
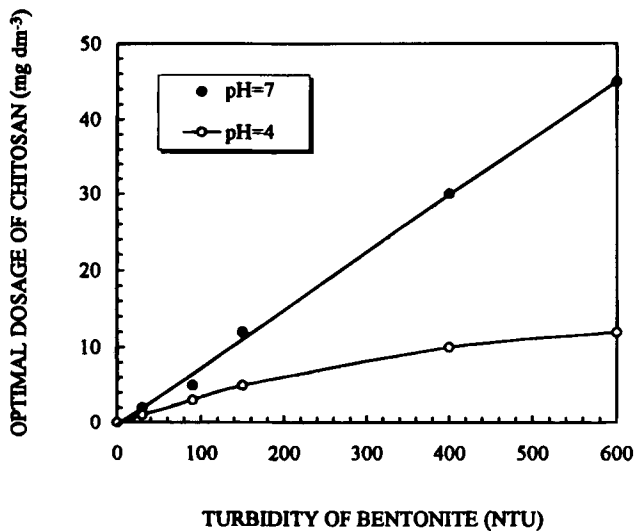
Fig. 3. Optimal chitosan dosages for bentonite suspensions of various turbidities in acidic and neutral pH conditions.
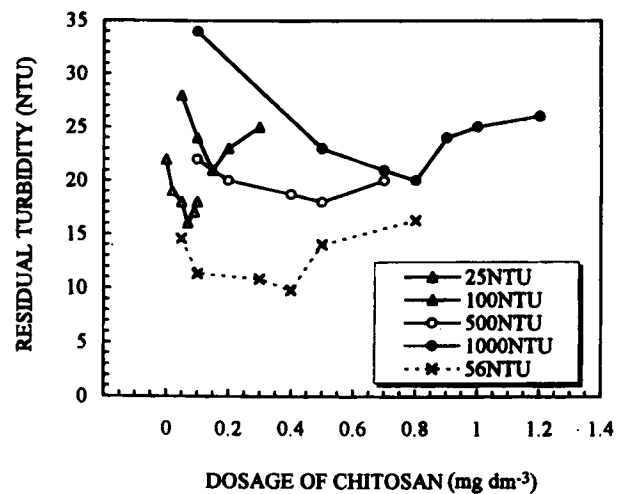

Fig. 4. The residual turbidities of supernatant after jar-mixing/settling with various chitosan dosages for the 25 NTU, 100 NTU, 500 NTU and 1000 NTU kaolinite suspensions and a 56 NTU raw suspension.

not proportional to the initial turbidities of suspension. The mechanism of alum coagulation at neutral pH is charge neutralization and enmeshment, or only enmeshment.[16] Excess coagulant is required in water of low turbidity to create the probability of chemical–particle collision and to produce a large excess of amorphous hydroxide precipitate, and conversely, a lesser dosage is required for highly turbid water.[15] Therefore, this suggests that chitosan has an advantage over the common coagulants with respect to the ease in determining the optimal dosage for coagulation on the basis of water turbidity.

3.3 Jar-mixing/settling for kaolinite and raw suspensions

An investigation was also made into the change in residual turbidity with the dosage of chitosan for kaolinite suspensions of 25 NTU, 100 NTU, 500 NTU and 1000 NTU. These results are presented in Fig. 4. The change in residual turbidity with the dosage of chitosan for a raw suspension of 56 NTU is also included in this figure. This figure reveals that the kaolinite and raw suspensions can be coagulated with chitosan. However, despite the initial turbidity of the kaolinite and raw suspensions, there are high residual turbidities for these suspensions with respect to the optimal chitosan dosage condition. This same figure shows that the efficiency of chitosan coagulation decreases with a decrease in kaolinite concentration. This decrease would imply that the coagulation behavior of kaolinite and natural particles by chitosan is different from that of bentonite particles. These particles are different in particle size, surface properties, and surface structure, to which may be attributed the difference in the effectiveness of coagulation. Hence, it is suggested that the

source and properties of clay particles in raw water exert a significant influence on the chitosan coagulation efficiency.

3.4 Bentonite as coagulant aid

In this study, the interaction of kaolinite with chitosan coagulant was improved by applying bentonite particles as an aid in coagulation. A given quantity of bentonite was added to the kaolinite suspensions prior to the chitosan dosing. Next, the suspensions were agitated for 2 min. Figure 3 indicates that the optimal dosage ratio of bentonite and chitosan is around 100 : 1 (w/w). Hence, in this study, the amounts of bentonite accompanying the chitosan coagulation were chosen to satisfy this ratio for the kaolinite and raw suspensions. Figure 5 shows the change in residual turbidity with chitosan for kaolinite suspensions of 25 NTU, 100 NTU, 500 NTU and 1000 NTU and a raw suspension of 56 NTU. This figure reveals that the trends of the residual turbidity curves for kaolinite and raw suspension are theoretically similar to those for bentonite, i.e., residual turbidity decreases to a minimum, which is followed by an increase in residual turbidity with chitosan dosage. In the case of 25 NTU, the additive bentonite can obviously improve the removal efficiency of kaolinite suspension by chitosan coagulation, thereby resulting in the lowest turbidity in the supernatant from 15 NTU (without bentonite addition) down to 0·6 NTU (with bentonite addition). A comparison of the optimal chitosan and bentonite dosages with kaolinite suspensions of various turbidities is shown in Fig. 6. Similarly, from this comparison a linear correlation occurs between the optimal chitosan dosage and the initial turbidity of the kaolinite suspension.
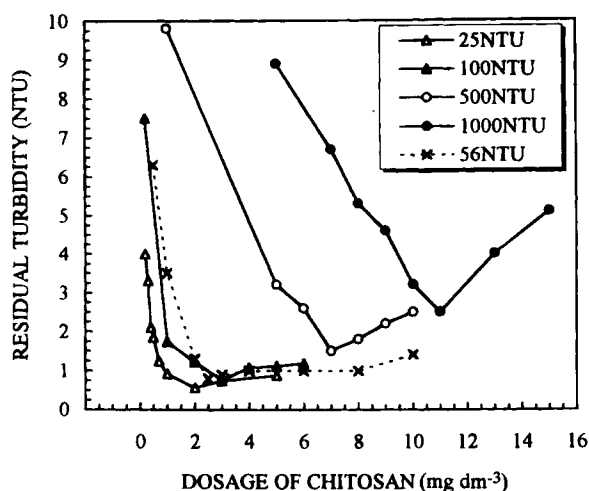
Fig. 5. The residual turbidities of supernatants after jar-mixing/settling with various chitosan dosages and bentonite additive for the 25 NTU, 100 NTU, 500 NTU, and 1000 NTU kaolinite suspensions and a 56 NTU raw suspension.

3.5 pH effect on the chitosan coagulation

In order to understand the relationship between the coagulation efficiency of chitosan and the pH value of raw water, the pH values of bentonite suspensions of 45 NTU have been adjusted to 4, 5, 6, 7, 8 and 9. The results obtained from jar-mixing/settling with 2 mg dm^{-3} chitosan are presented in Fig. 7. In the pH range of 5 to 7, the residual turbidities of the supernatant can be reduced to less than 1 NTU. In particular, a lowest turbidity of 0·42 NTU can be reached at pH 6. These results also indicate that the residual turbidities of supernatant are slightly increased at pH 4 or pH 8 and 9. Despite the wide pH range, the residual turbidities in this result are obviously all below 5 NTU. This would
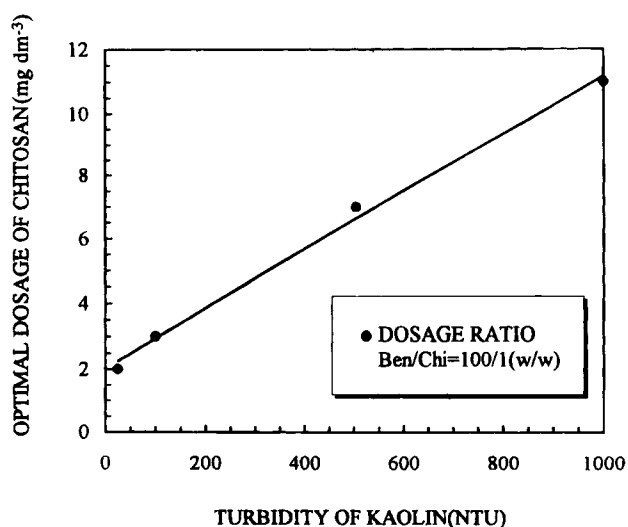

Fig. 6. The comparison of the optimal chitosan and bentonite dosage with kaolinite suspensions of various turbidities.
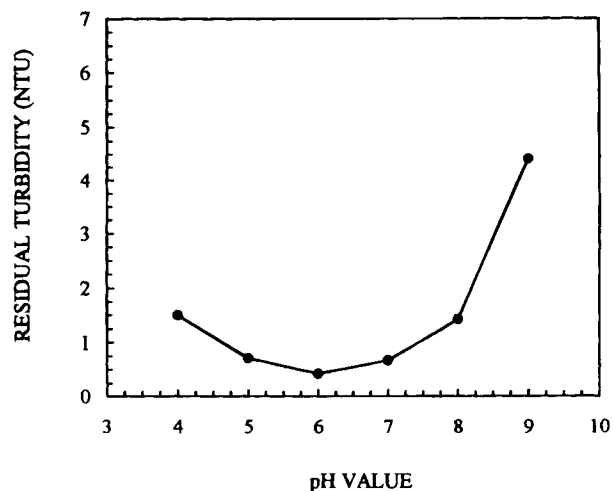

Fig. 7. The residual turbidity of bentonite suspensions after jar-mixing/settling as a function of pH (chitosan dosage = 2 mg dm^{-3}; initial turbidity = 45 NTU).

suggest that the coagulation efficiency of chitosan for colloids is only slightly influenced by the pH change. Therefore, chitosan dosage is the major parameter determining coagulation efficiency. According to Fig. 3, the optimal dosage is 1·8 mg dm^{-3} at pH 4 and 3·5 mg dm^{-3} at pH 7 for a 45 NTU bentonite suspension. Hence, 2 mg dm^{-3} of chitosan dosing at pH 4 barely reaches the range of overdosage. However, that dosage is insufficient for the optimal operation at pH values above 7. Therefore, as previously mentioned, the below-dosage at pH 4 and overdosage at pH 8 and 9 cause a slight increase in the residual turbidity of supernatants at pH 4, 8 and 9.

4 CONCLUSIONS

This study assessed the feasibility of the application of chitosan for the coagulation of colloidal particles. Chitosan is a potent coagulant for bentonite suspension, and its optimal dosage has a linear correlation with the turbidity of the source water. The optimal chitosan dosage at neutral pH is higher than that in the acidic condition for bentonite suspensions under the same initial turbidity. The coagulation behavior of kaolinite and natural particles by chitosan is different from that of bentonite particles. Chitosan fails to form a good aggregate with kaolinite or with natural particles. Therefore, the source and properties of clay particles in raw water have a great influence on the coagulation efficiency of chitosan. It is suggested that turbid water containing particles similar to kaolinite need to have some bentonite particles added as a coagulant aid; this clearly improves the removal efficiency of kaolinite suspension by chitosan coagulation. The pH effect on the coagulation efficiency of chitosan is insignificant. The evidence infers that charge neutralization is not a major

mechanism controlling the formation of floc for chitosan coagulation.

REFERENCES

1. Tanne, J. E., Alzheimer and aluminum—an element of suspicion. *Amer. Health*, **48** (1983) 165–73.
2. Letterman, R. D., Modeling the effect of hydrolyzed aluminium and solution chemistry on flocculation kinetics. *Env. Sci. Tech.*, **19** (1985) 673–81.
3. Martin, C. N., Osmond, C., Edwardson, J. A., Barker, D. J. P., Harris, E. C. & Lancey, R. F., Geographic relation between Alzheimer's and aluminum in drinking water. *The Lancet*, **1** (1989) 59–65.
4. Hanson, H., Perler, A. & Saxena, J., The regulatory framework for the control and use of organic polyelectrolytes in drinking water. *AWWA Sunday Seminar, Proc. AWWA Ann. Conf.*, Las Vegas, 1983.
5. Knorr, D., Wampler, J. P. & Teutonico, R. A., Formation of prazine by chitin pyrolysis. *J. Food Sci.*, **50** (1985) 1762–71.
6. Graziella, D. P., Francoise, L. & Roland, A., Flocculation and adsorption properties of cationic polyelectrolytes toward Na-Montmorillonite dilute suspensions. *J. Colloid and Interface Science*, **119** (1987) 474–80.
7. Mangravite, F. J., Synthesis and properties of polymers used in water treatment. *Proc. AWWA Sunday Seminar, Use of Organic Polyelectrolytes in Water Treatment AWWA*, Denver, CO, 1983.
8 Halverson, F. & Panzer, H. P., Flocculating agents. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 10, 3rd edn. John Wiley, New York, 1980.
9. Aizawa, T., Magara, Y. & Musashi, M., Problems with introducing synthetic polyelectrolyte coagulants into the water purification process. *Water Supply*, **9** (1991) 27–35.
10. Bartby, J., Toxicity of synthetic polyelectrolytes. In *Coagulation and Flocculation*. Upland Press, Ltd, UK, 1980, pp. 88–89.
11. Letterman, R. D. & Pero, R. W., Contaminants in polyelectrolytes used in water treatment. *J. AWWA*, **82** (1990) 87–97.
12. Parazak, D. P., Burkhardt, C. W., McCarthy, K. J. & Stehlin, M. P., Hydrophobic flocculation. *J. Colloid and Interface Science*, **123** (1988) 59–72.
13. Domard, A., Rinaudo, M. & Terrassin, C., Adsorption of chitosan and a quaternized derivative on kaolinite. *J. Applied Polymer Science*, **38** (1989) 1799–806.
14. Kawamura, S., Effectiveness of natural polyelectrolytes in water treatment. *J. AWWA*, **10** (1991) 88–91.
15. Weber, W. J. Jr, *Physicochemical Processes*. John Wiley, New York, 1972.
16. Dentel, S. K., Coagulation control in water treatment. *Critical Rev. in Env. Control*, **21** (1991) 41–135.